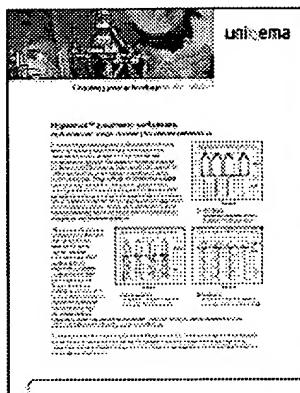


Hypermer™ polymeric surfactants

High molecular weight chemistry for ultimate performance



Uniqema's Hypermer polymeric surfactants are molecules featuring repeating hydrophilic and hydrophobic units, designed to produce emulsions of high stability and controllable droplet size. The range of Hypermer products contained in this literature has been specifically selected for oilfield applications, where highest emulsification performance is required. Responding to the diverse technologies used in drilling, completion, stimulation, production and cleaning applications, Uniqema's Hypermer range of oilfield surfactants combine a number of innovative base chemistries and emulsification mechanisms to readily produce water-in-oil or oil-in-water emulsions. All use steric stabilization to form thermodynamically stable emulsions controlling flocculation, coagulation and coalescence effects.

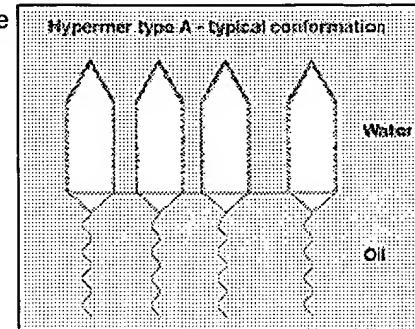
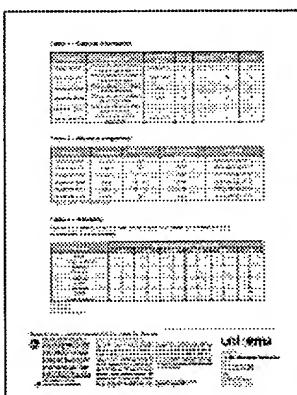


Figure 1

A - PEG Alkyds

Hydrophobe: Long-chain alkylene
Hydrophile: Polyethylene glycol



These base chemistries of Hypermer surfactants are highly efficient interfacially active agents, yet they only marginally affect surface tension. Hypermer polymeric surfactants are non-ionic, however, the E type variant can behave as an anionic in suitably basic conditions. Hypermer surfactants are resistant to high ion concentrations, dispersed phase volumes and temperatures, meaning that highly stable emulsions can be produced with minimal foaming, even in paraffinic oils.

Following is a list of Uniqema's polymeric surfactants from the Hypermer range currently available for use in the oil and related industries. The generic chemistry, physical state and regulatory status are indicated. Please consult your local Uniqema representative for product lead times and for additional information.

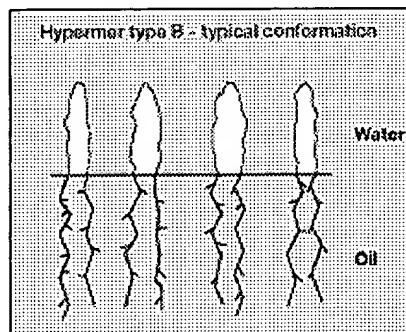


Figure 2

B-Block copolymer

Hydrophobe: Polyhydroxy fatty acid
Hydrophile: Polyethylene glycol

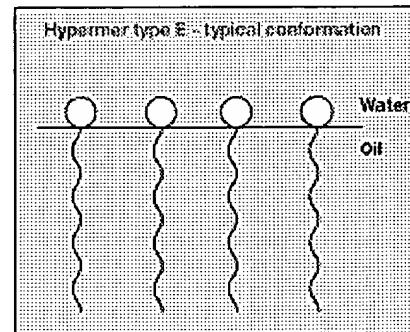


Figure 3

E-Oligomers

Hydrophobe: Long-chain alkylene
Hydrophile: Anionic/nonionic (various)

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FILE COVERS 1907 - 24 Apr 2003 VOL 138 ISS 17
FILE LAST UPDATED: 23 Apr 2003 (20030423/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s hypermer (P) 464
200 HYPERMER
1 HYPERMERS
201 HYPERMER
(HYPERMER OR HYPERMERS)
3959 464
L1 2 HYPERMER (P) 464

=> s l1 and pluronic
4657 PLURONIC
269 PLURONICS
4755 PLURONIC
(PLURONIC OR PLURONICS)
L2 1 L1 AND PLURONIC

=> d 12 ti

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
TI Stable invert fuel emulsion compositions and method of making

=> d 12 all

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
AN 1999:784208 CAPLUS
DN 132:13709
TI Stable invert fuel emulsion compositions and method of making
IN Coleman, Gerald N.; Endicott, Dennis L.; Jakush, Edward A.; Nikolov, Alex
PA Caterpillar Inc., USA
SO PCT Int. Appl., 39 pp.
CODEN: PIXXD2
DT Patent
LA English
IC ICM C10L001-32
CC 51-7 (Fossil Fuels, Derivatives, and Related Products)
FAN.CNT 1
PATENT NO. KIND DATE APPLICATION NO. DATE
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PI WO 9963024 A1 19991209 WO 1999-US12199 19990601
 W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE,
 DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP,
 KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO,
 NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA,
 UG, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
 RW: GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW, AT, BE, CH, CY, DE, DK,
 ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG,
 CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG
 AU 9942280 A1 19991220 AU 1999-42280 19990601
 PRAI US 1998-88060P P 19980605
 US 1998-88060 P 19980605
 WO 1999-US12199 W 19990601

AB Method for producing high stability aq. fuel emulsions with an oil or fuel continuous phase. The method provides for selectively combining prescribed quantities of diesel fuel, purified water, alc., and an additive package including a primary surfactant, a block copolymer, and a polymeric dispersant. The fuel emulsion is made by blending the diesel fuel and additive package, adding purified water to the fuel/additive mixt., aging the compn., and passing the aged compn. through a high shear mixer. The optimum stability in the oil continuous fuel emulsion is achieved by using a high shear mixing device, such as a Ross X-series Mixer Emulsifier, which results in the final fuel emulsion having a droplet size distribution of .apprx.1 .mu. or less.

ST diesel fuel emulsion
IT Polymers, uses
 RL: MOA (Modifier or additive use); USES (Uses)
 (block; stable invert fuel emulsion compns. and method of making)

IT Diesel fuel
 Dispersing agents
 Fuels
 Surfactants
 (stable invert fuel emulsion compns. and method of making)

IT Fatty acids, uses
 RL: MOA (Modifier or additive use); USES (Uses)
 (stable invert fuel emulsion compns. and method of making)

IT Gasoline
 RL: PEP (Physical, engineering or chemical process); PROC (Process)
 (stable invert fuel emulsion compns. and method of making)

IT 93-83-4 106392-12-5, Pluronic 17R2 154101-90-3,
Hypermer E-464
 RL: MOA (Modifier or additive use); USES (Uses)
 (stable invert fuel emulsion compns. and method of making)

RE.CNT 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE
 (1) Bertha Andras; WO 9812285 A 1998 CAPLUS
 (2) British Petroleum Co PLC; EP 0301766 A 1989 CAPLUS
 (3) Entoleter; WO 7900211 A 1979 CAPLUS
 (4) Gunnerman Rudolf, W; WO 9527021 A 1995 CAPLUS
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 (6) Peter-Hoblyn Jeremy, D; US 5584894 A 1996 CAPLUS
 (7) Scheuermann Ted, W; US 5873916 A 1999 CAPLUS

=> FILE REG

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Experimental and calculated property data are now available. See HELP
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in the CAS Registry File, for complete details:
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L3 1 154101-90-3/RN

5

The ethyl alcohol combusts and the carbamic acid produced insitu decomposes readily to ammonia and carbon dioxide. The ammonia reduces the oxides of nitrogen. The ethyl carbamate is a component of the microemulsion fuel. The key to this concept is that the ammonia is produced in the later stages of the combustion which is desirable.

(c) Use a combination of (a) and (b).

3. The concept that the sulfur in petroleum products such as diesel oil and fuel oil oxidize to sulfur oxides like sulfur dioxide in the combustion chamber and the sulfur oxides combine with steam in the exhaust gases to produce sulfur acids such as sulfurous acid which pollutes the air. Further to this concept is that the combination of oxides of nitrogen and the sulfur acids result in acid rain which is detrimental to vegetation.

The idea created is to stoichiometrically neutralize the sulfur acids generated in the combustion chamber by adding an alkaline substance like sodium bicarbonate or sodium carbonate to the microemulsion fuel.

The above objectives of this invention and the above concepts and ideas to achieve these objectives are embodied in the new and novel microemulsion fuel compositions by weight which are summarized as follows:

(a) Diesel oil or fuel oil comprising about 50 to 90% of the 25 microemulsion fuel.

(b) An anionic surfactant prepared from the partial neutralization of 60 to 70 mole percent of the unsaturated fatty acids with ammonia such that there results both free fatty acids and the ammonium salts of the fatty acids. The ammonium salts of the fatty acids which represent the anionic surfactant comprise about 4 to 12% by weight of the 30 microemulsion fuel. The free fatty acids comprise about 2 to 6% by weight of the microemulsion.

(c) A non-ethoxylated non-ionic surfactant. The specific surfactant, which is a novel part of this invention, is 2,4,7,9-tetramethyl-5-decyne-4,7 diol, manufactured by Air Products and Chemicals, Inc. under the trade name of Surfynol 104. When this surfactant is dissolved in 2-ethylhexanol-1 as a 50% solution by weight it is called Surfynol 104A. The surfactant and the solvent comprise about 1 to 2% each by weight of the microemulsion. This surfactant is also called "Acetylenic Diol Surfactant" which name will be used in the examples.

(d) Long chain water-insoluble or slightly soluble in water aliphatic alcohols with melting points below 0° C., for example, octanol-1, comprising 2 to 8% by weight of the 45 microemulsion.

(e) The sodium salts of the fatty acids to stoichiometrically neutralize the sulfur acids generated from the oxidation of sulfur in diesel oil or fuel oil during combustion with the amount of the sodium salts comprising about 0.2 to 0.5% by weight of the microemulsion fuel. The amount of sodium salts required is dependent on both the sulfur content of the diesel oil and fuel oil and also, the percentage of diesel oil 50 or fuel oil used in the microemulsion fuel.

(f) Water-soluble aliphatic alcohols such as methanol and ethanol comprising about 5 to 14% of the microemulsion fuel.

(g) Total water in the microemulsion comprising about 1 to 10% of the microemulsion fuel.

(h) Urea NO_x scavenger comprising about 0.1 to 4.0% by weight of the microemulsion fuel.

(i) Ethyl carbamate NO_x scavenger comprising about 0.1 to 4.0% by weight of the microemulsion fuel.

The first step in the preparation of the water-in-oil microemulsion fuel is to prepare the solution of additives. In

6

preparing this solution there is no particular order of adding the components except that the aqueous ammonia is added last. However, there is one exception to this. For solutions containing ethyl carbamate, the aqueous ammonia is added before the ethyl carbamate to assure that none of the ethyl carbamate will hydrolyze.

The second step is the mixing of the solution of additives with the petroleum product such as diesel oil. One of the advantages of the microemulsions of this invention is that only very low shear mixing is necessary to prepare the water-in-oil microemulsion fuels.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to low viscosity, stable (W/O) microemulsions prepared by mixing petroleum products such as diesel oil and fuel oil with a solution of additives. The microemulsions are crystal clear at room temperature but like diesel oil and heating fuel oil, they become hazy at sub-freezing temperatures but with the important characteristics that there is not any phase separation and that they have good fluidity like diesel oil itself.

The solution of additives is a clear, low viscosity and stable molecular solution. It is prepared separately and can be stored separately until ready to use when preparing the microemulsions fuel.

The microemulsion is readily prepared by mixing the petroleum product with the solution of additives at room temperature. On a large scale the microemulsion can be prepared by feeding the solution of additives and the petroleum product from the respective storage tanks through separate pipe lines into a common pipe line that leads to a storage tank for the microemulsion fuel. The flow rates are monitored to deliver the preferred blend of the solution of additives with the petroleum product. For example, a preferred blend of v/v 65/35 diesel oil/additive solution is continuously prepared in which the flow rate of the diesel oil is 1.857 times the flow rate of the solution of additives for the same pipe diameter. The flow rates are readily maintained because of the low viscosities and easy transport of both the solution of additives and the diesel oil.

THE FUNDAMENTAL COMPONENTS OF THIS INVENTION

The solution of additives comprise six fundamental components described below.

1. An anionic surfactant prepared by the neutralization of 60 to 70% of the unsaturated fatty acids with ammonia such that there results both the ammonium salts of the fatty acids which represent the anionic surfactant and free fatty acids.

2. A non-ethoxylated non-ionic surfactant, the acetylenic diol surfactant, 2,4,7,9-tetramethyl-5-decyne-4,7-diol dissolved in 2-ethylhexanol-1.

3. Long chain, water-insoluble aliphatic alcohols with melting points below 0° C. such as octanol-1.

4. Water-soluble aliphatic alcohols such as methanol and ethanol.

5. Water.

6. NO_x scavengers urea and ethyl carbamate..

Item 1

Unsaturated fatty acids derived from vegetable oils such as soybean oil which consist of oleic acid, linoleic acid and linolenic acid which comprise at least 90% of the fatty acids are used. Present in the unsaturated fatty acids are minor

1.36?